

Polymer transport across isotope-selective interdiffusion barriers

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Abstract. – Neutron reflectivity experiments were performed to study the interdiffusion of two compatible polymers, polystyrene and deuterated polystyrene, across a free-standing ultra-thin (60 Å) interstitial membrane. Annealing above the glass transition temperature and quenching back to room temperature allows for a time-dependent study of the changing concentration profile due to membrane-mediated interdiffusion. For the case of matched polymer molecular masses but different isotopic labeling, faster transport of the deuterated polymer across the interstitial layer is observed leading to displacement of the membrane. Varying the molecular mass and isotopic labeling of the top polymer layer provides information about the size discrimination and isotopic selectivity of the membrane.

Currently, a tremendous technological and scientific effort is being invested in scaling down feature sizes in modern devices, *e.g.* microelectronics or hybrid materials such as polymer based microelectronics [1]. New materials on nanometer scales are based on combinations of components with different molecular properties. One of the immediate consequences is the need to understand and control interfaces between different materials as the material properties are largely governed by interfacial phenomena. The well-known Kirkendall effect [2] in metal composites, dewetting phenomena of metallic or polymeric films on surfaces [3], adsorption phenomena in polymer blend thin films [4, 5] or controlled drug release through barrier layers [6] are common examples of similar phenomena in very different fields. While interdiffusion of compatible materials [7] and the partial interpenetration of incompatible materials (“interfacial width”) [8] were thoroughly studied, the effects of an interstitial barrier layer, sandwiched between two compatible materials, on interdiffusion is a less understood problem both experimentally and theoretically [9, 10]. Here, we present a study of a diffusion barrier formed by a polymeric nanometric membrane between two polymer layers.

The interdiffusion of two compatible polymers of equal and different molecular masses was thoroughly investigated using a variety of different techniques [11–16]. The aim of those experiments was to test theoretical models dealing with polymer dynamics as a function of

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TABLE I – Molecular masses, $M_{w,n}$, and degree of polymerization, P , of the polymers used. hPS(22 k, 36 k) and dPS(49 k) were obtained from Polymer Source, Inc.; all other polymers are from Polymer Laboratories, Inc. The error of the measured GPC values is around 4%.

Code	Stated			Measured		
	$M_w/(\text{kg/mol})$	M_w/M_n	P	$M_w/(\text{kg/mol})$	M_w/M_n	P
hPS(22 k)	22.2	1.07	213	24.0	1.03	231
hPS(28 k)	28.5	1.03	274	28.1	<1.03	270
hPS(36 k)	36.0	1.06	346	38.1	1.03	366
hPS(39 k)	39.0	1.02	375	37.5	<1.03	361
dPS(27 k)	27.0	1.02	241	25.6	<1.03	229
dPS(40 k)	40.0	1.02	357	40.2	<1.03	359
dPS(49 k)	49.0	1.03	438	47.9	<1.03	428

molecular mass. Typically, polymer interdiffusion in polymer bilayers was monitored. Some of these methods monitored the evolution of the interdiffusion profile with time through isotopic labeling of one polymer to provide an analytical contrast. Other methods relied on the placement of markers at the initial interface and traced their displacement during polymer interdiffusion for mismatched polymer molecular mass [11,12,16–19]. The latter studies assume that the markers are inert and do not affect the polymer interdiffusion in order to extract the diffusion coefficients for the system. However, some recent work shows that gold particles can be bridged by interactions with the polymers resulting in a retardation of both the gold particle and polymer mobility [18]. In a series of experiments using polymers of different molecular masses and isotopic labeling we show that interdiffusion is altered by the presence of an interacting ultrathin membrane at the polymer/polymer interface. Furthermore, our results open new questions about the interpretation of previously reported marker experiments.

In this letter, we present a detailed study of polymer melt interdiffusion for two compatible polymers A and B across a non-porous incompatible ultra-thin interstitial membrane M. Initial results were published recently [20]. Here, polymers A and B are polystyrene, PS, of different weight average molecular mass M_w and isotopic labeling. The membrane material is isopentylcellulose cinnamate (IPCC). The preparation of this trilayer sample requires 3 steps. First, the polymer A layer (thickness $d \sim 500$ Å) is spin-coated from a toluene solution on a clean hydrophobic silicon (Si) wafer (for experimental details, see [20]) and is subsequently annealed for 2 h at $T = 120^\circ\text{C}$. Second, six monolayers of IPCC ultra-thin films were transferred on top of the spin-coated layer of polymer A using the Langmuir-Blodgett technique, and subsequently photo crosslinked using UV light with a wavelength $\lambda > 280$ nm to create a 60 Å membrane network. Third, the polymer B layer (thickness $800 \text{ Å} < d < 1000 \text{ Å}$) was floated on top of these two layers to form the model trilayer sandwich system Air//Polymer B/M/Polymer A//Si. The complete trilayer was then annealed under vacuum at 80°C for at least 2 h. In all cases, perdeuterated polystyrene with a molecular mass of $M_w = 40$ k (k = kg/mol) serves as polymer A, while the molecular mass as well as the isotopic labeling of polymer B are varied. Table I contains the molecular masses and isotopic labeling for the different polymers serving as layer B. Neutron reflectivity (NR) measurements were taken with quenched samples to monitor changes in the depth profile upon annealing at $T = 120^\circ\text{C}$ for different times. The NR data were obtained on the NG7 reflectometer at the NIST Center for Neutron Research. The instrumental resolution, wavelength and accessible q -range are $dq/q \simeq 0.045$, 4.75 Å, and $0\text{--}0.24$ Å⁻¹, respectively. Fitting of the NR data was carried out using a standard multilayer fitting routine [21].

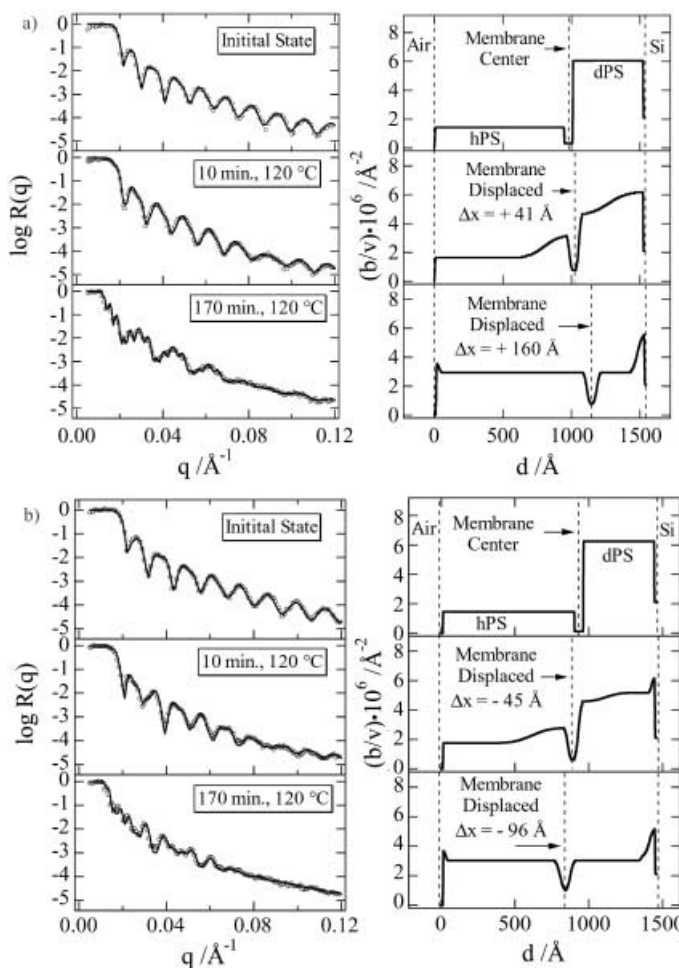


Fig. 1 – Neutron reflectivity data as a function of q (q , scattering vector; $q = 4\pi/\lambda \cdot \sin \theta$; λ , neutron wavelength with $\lambda = 4.76$ Å; θ , scattering angle) taken at three different annealing times. At lower q ($q \leq 0.08$ Å⁻¹) the standard deviation is smaller than the symbol size; at highest q it corresponds to half a decade on the log scale. The right-hand side shows the corresponding SLD profiles used to fit the NR data. (a) Air//hPS(39 k)/60 Å IPCC/dPS(40 k)//Si; (b) Air//hPS(22 k)/60 Å IPCC/dPS(40 k)//Si.

Figure 1(a) shows typical NR data taken with a matched molecular mass pair of PS but different isotopic labeling, *i.e.* Air//hPS(39 k)/60 Å IPCC/dPS(40 k)//Si, for three annealing times. The right side shows the corresponding scattering length density (SLD) profiles used to fit the NR data. Upon annealing for, *e.g.*, 10 min at $T = 120$ °C, the membrane is displaced towards the Si interface (arbitrarily defined as the positive direction) indicating a shrinkage of the dPS layer and thus faster transport of the dPS through the membrane relative to hPS in the opposite direction. The membrane displacement stops at a final displacement Δx_f , the difference between the initial and final positions of the membrane relative to the silicon wafer, once the concentration gradient across the membrane relaxes. The membrane itself swells from an initial thickness of 60 Å to a thickness of 110 Å after 10 minutes. Furthermore, an enrichment of dPS at the air and Si interface is observed. While the dPS enrichment at the air

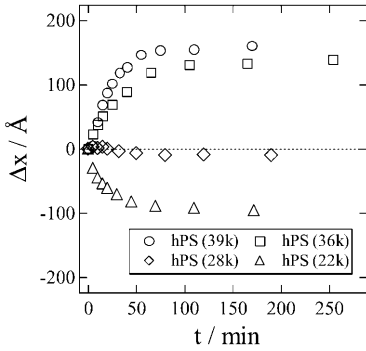


Fig. 2

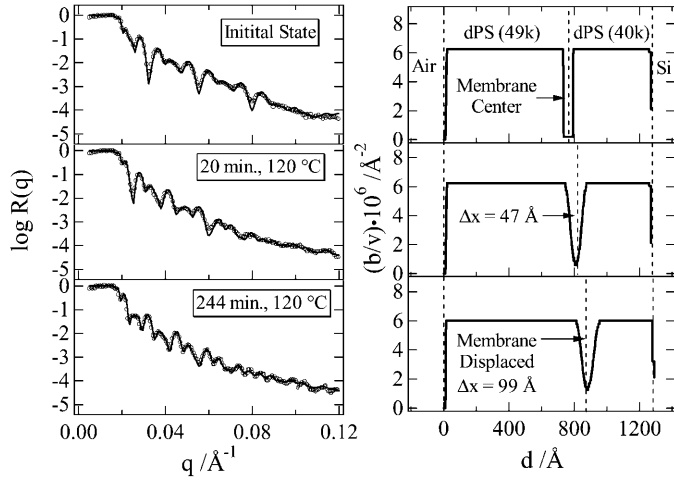


Fig. 3

Fig. 2 – Membrane displacement kinetics using variable-molecular-mass hydrogeneous polystyrene as the top layer, B and 40 k dPS as the bottom layer, A.

Fig. 3 – NR data for Air//dPS(49 k)/60 Å IPCC/dPS(40 k)//Si. See fig. 1 for an explanation.

interface was observed before [22], the dPS enrichment at the Si interface is probably a kinetic effect as the mobility next to the Si surface is decreased [23]. Earlier experiments showed that the magnitude and kinetics of membrane displacement are the same for the reversed configuration Air//dPS(40 k)/60 Å IPCC/hPS(39 k)//Si but with the membrane moving in the opposite direction (negative direction) [20]. As both polymers are of matched molecular mass, this finding implies faster transport of the deuterated polymer and thus isotopic discrimination by the membrane. To separate size exclusion from isotopic effects, a series of experiments were performed where the molecular mass of the hPS top layer B was systematically varied while the molecular mass of the bottom layer was held constant by always using dPS(40 k). Figure 1(b) shows a series of three different annealing times for an experiment using a much smaller hPS sample as the polymer B layer, *i.e.* Air//hPS(22 k)/60 Å IPCC/dPS(40 k)//Si. Upon annealing, the membrane now travels towards the air interface reflecting a faster net transport of the smaller hPS over the bigger dPS. Figure 2 shows the kinetics of membrane displacement for different molecular masses of hPS serving as layer B. The displacement kinetics can be fit using single exponential functions which level off at the final membrane displacement Δx_f . As can be seen in fig. 2, the membrane displacement is almost balanced by using hPS with a molecular weight of $M_w = 28$ k where faster transport due to the smaller molecular size just balances the faster transport due to the deuterium labeling. NR can also probe the membrane displacement in samples where both polymer layers A and B consist of deuterated polymers. As both polymers are deuterated, the displacement reflects only the effect of polymer size on the tranport rates across the membrane. Figure 3 shows a typical experimental data set for a sample Air//dPS(49 k)/60 Å IPCC/dPS(40 k)//Si. The membrane displacement towards the Si side indicates faster net transport of the smaller dPS(40 k) polymer across the membrane. The kinetics of membrane displacement for perdeuterated top layer samples is shown in fig. 4. The experiment using the same polymer dPS(40 k) on both sides of the membrane reveals no displacement within the experimental resolution ± 5 Å. The kinetics and direction of the membrane displacement in perdeuterated systems is purely

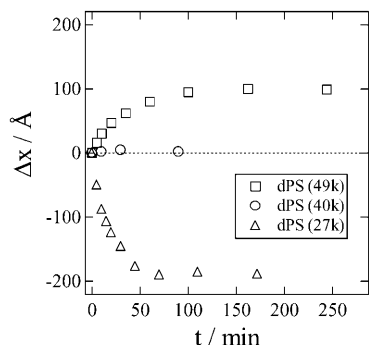


Fig. 4

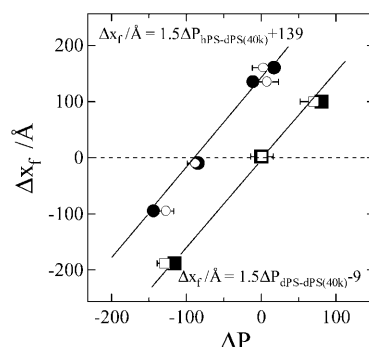


Fig. 5

Fig. 4 – Kinetics of membrane displacement using perdeuterated polystyrene with variable molecular mass as a top layer, B, and 40 k dPS as the bottom layer, A. The error for the membrane position is ca. ± 5 Å.

Fig. 5 – Final membrane displacement Δx_f as a function of difference in degree of polymerization between the top polymer layer, B, of variable P and the reference bottom polymer layer, A = dPS(40 k) with $P = 357$; filled symbols: ΔP calculated using manufacturer data; open symbols: ΔP calculated using the measured GPC data. The linear fits are based on manufacturer's data.

determined by the size difference of the polymers serving as layer A and B. Figure 5 shows the final membrane displacement Δx_f for hPS/M/dPS and dPS/M/dPS experiments, respectively, plotted as a function of differences in the weight average degree of polymerization ΔP between the top layer polymer B and the reference polymer A, dPS(40 k) of $P = 357$ repeat units. The final displacement Δx_f depends linearly on ΔP but the line for the hPS/M/dPS experiments is shifted towards smaller ΔP due to the isotopic effect. The slope of both lines is the same, 1.5 Å per unit monomer difference indicating strong “size discrimination” by the membrane. Figure 5 clearly shows that the membrane is isotope-selective and leads to faster transport of the deuterium-labeled polymer over its protonated homologue through the barrier layer. As the transport through the membrane exhibits a strong molecular-mass dependence, the faster transport of deuterated PS can be balanced by hPS that is 80 repeat units shorter. By using even smaller molecular weight masses, the isotope effect can be overcome to reverse the displacement direction.

To further understand the membrane's effect on polymer interdiffusion, bilayer interdiffusion experiments without the membrane were carried out using the same polymers, *e.g.* Air//hPS(28k)/dPS(40k)//Si and Air//hPS(39 k)/dPS(40 k)//Si. The annealing temperature for these experiments was lowered to $T = 103$ °C to allow for a detailed study of the initial broadening of the interfacial width by NR. For the chosen early annealing times, no reflection at any interfaces occurs. The interfacial profile is fit using a single error function. Neither experiment revealed a change of the dPS layer thickness of more than 5 Å. The mutual diffusion coefficient of the hPS(28 k)/dPS(40 k) experiment is about 30% larger, reflecting the faster diffusion of the lower-molecular-weight species in this mismatched molecular-mass case. Theoretically, one would expect the interface to move in finite bilayer systems for unequal layer thickness in the moment where reflection at one interface occurs [24], causing the thicker layer to shrink. Unfortunately, NR only allows us to see the early stages of interdiffusion as it is insensitive to the large interfacial widths observed for intermediate and late times for miscible bilayers just prior to the formation of a homogeneous mixed sample. Nonetheless, in our membrane experiments, we observe the opposite behavior, *i.e.* a shrinking of the thinner

dPS layer. These results show that the displacement of the membrane, which can be as large as 160 Å for the cases considered, is clearly caused by the interplay of specific interactions and inherent diffusivities between the polymers and the membrane material.

This study of membrane-mediated polymer interdiffusion across a free-standing membrane shows that the transport of polymers depends on the size and isotopic labeling of the polymer. The driving force for this transport is the gradient in chemical potential of each species, μ_i , across the membrane leading to a flux $j_i = M_i \cdot \nabla \mu_i$ [7], with M_i being the Onsager transport coefficients. The transport process can be divided into three steps assuming a solution-diffusion-type mechanism: 1) sorption of the polymer into the membrane material, 2) diffusion through the membrane, and 3) desorption at the other side of the membrane. Therefore, the permeability is a function of solubility and diffusivity with both affecting the selectivity of the membrane. Membrane selectivity, in our case for size and different isotopes, is obtained because of one component's ability to cross the membrane more easily. At this stage of the study it is impossible to assign a molecular mechanism for this amazing degree of selectivity; nonetheless, it seems intuitive that the size discrimination is probably caused by a larger transport coefficient for the smaller polymers in the membrane material. To explain the isotopic selectivity, dPS must have either a higher solubility or a larger transport coefficient compared to its protonated analogon of equal molecular mass. As polystyrene and IPCC represent a hairy-rod/coil blend, they can be expected to have a complex phase diagram with an upper critical solution temperature [25]. It was already observed in the system hPS/PVME that isotopic labeling of PS can lead to a considerable shift of the critical temperature [26]. A shift of the hPS/IPCC phase diagram upon switching to dPS/IPCC would explain a different diffusion coefficient and/or a different solubility of dPS inside the IPCC membrane compared to hPS. In terms of a generalized solution-diffusion type transport mechanism [27], three Flory-Huggins interaction parameters determine the chemical potential of each species inside the membrane, $\chi_{\text{hPS/IPCC}}$, $\chi_{\text{dPS/IPCC}}$, $\chi_{\text{hPS/dPS}}$, and therefore the selectivity. As the Flory-Huggins parameter $\chi_{\text{hPS/dPS}}$ is substantially smaller than the critical interaction parameter for all molecular weights used here, the conclusion of our experiment is that the Flory-Huggins interaction parameters $\chi_{\text{hPS/IPCC}}$ must be bigger than $\chi_{\text{dPS/IPCC}}$. To further investigate the origin of the different interaction, experiments with partially deuterated polymers will be performed.

While our findings might seem related to the classical Kirkendall effect and to polymeric marker experiments, the origin of the phenomena observed here is different. For matched molecular weights of dPS and hPS, the tracer diffusion coefficients are essentially the same, $D_A = D_B$. In metallic and polymeric marker systems no displacement of the interfacial plane was observed for the case of equal diffusion coefficients, while we observe a large membrane displacement. The different interactions with the membrane which would be regarded as inert in a marker experiment, results in different transport rates for A and B through M. Another experiment which clearly demonstrates that the different transport rate of A and B through M drives the membrane displacement is the interdiffusion of 28 k hPS and 40 k dPS, through the IPCC membrane, Air/hPS (28 k)/60 Å IPCC/dPS (40 k)/Si. In this experiment, the tracer diffusion coefficients are clearly different, $D_B < D_A$. If the mechanism were the same as the Kirkendall or polymeric marker experiments, a displacement of the interface both with and without the membrane would be expected. Clearly, membrane displacement is not observed for the membrane-mediated interdiffusion. The fact that no displacement of the interfacial plane was observed in the standard interdiffusion experiment (no membrane) using mismatched molecular masses raises the question of whether the markers are completely inert or are sensitive to molecular mass to a certain degree.

In summary, a series of experiments shows displacement of a free-standing ultra-thin mem-

brane (60 Å) sandwiched between two polystyrene layers upon annealing above the glass transition temperature. The direction and kinetics depend on the diffusants molecular mass and isotopic labeling, resulting in remarkable size and isotopic selectivity by the membrane. The size discrimination can be rationalized by assuming a faster diffusion coefficient for smaller polymers inside the membrane material while the isotopic selectivity appears to originate from a more favorable Flory-Huggins interaction parameter for dPS/IPCC compared to hPS/IPCC, which is another manifestation of unusual isotopic effects in polymeric systems. Though IPCC and PS are strongly incompatible, significant transport across this ultra-thin IPCC interdiffusion barrier occurs due to the nanoscopic thickness of the barrier layer which is comparable to the radius of gyration of the polymers. This finding is of general importance for the future design of polymeric multilayer devices.

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